Tracking the fate and transport of estrogens following rainfall events
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ABSTRACT

Surface runoff following rainfall events can transport estrogens from agricultural land to water systems, causing potential risks to aquatic biota. This study adopted two simple models, the wash-off and empirical models, to quantify the pathway of three prevalent manure-borne estrogens, estrone (E1), 17β-estradiol (E2β) and 17α-estradiol (E2α), from agricultural land to the receiving water following rainfall events. The complex interconversion of the three estrogens during attenuation was considered in the models. These two models were calibrated and validated using the data obtained from three artificial rainfall events from the literature. The data from the first two rainfall events were used to quantify key model parameters and the data from the third rainfall event were used to validate the models. The performances of the models were then evaluated through a statistical analysis. Results show that both models can closely reproduce the mass loads of estrogens during rainfall events and that the wash-off model shows a better overall performance than the empirical model for the data used in this study.

Key words | dynamics, estrogen, model, wash-off

INTRODUCTION

Estrogens raise many concerns once they are released into the environment as they can disturb the normal reproductive functions of aquatic animals (Brion et al. 2004; Kidd et al. 2007). Farm animals generate large amounts of hormones including estrogens through metabolic processes and excrete them through urine and feces (Lange et al. 2002; Raman et al. 2004). For example, one cow and one boar can excrete 299 μg and 2,300 μg of estrogens per day, respectively (Lange et al. 2002). Livestock wastes are frequently used as fertilizers for cropland and pastures, contributing large amounts of estrogens onto agricultural land (Chen et al. 2010; Zhao et al. 2010). In addition to livestock animals, biosolids, which contain estrogens, act as an additional source of estrogens onto agricultural land through land application (Andaluri et al. 2012). One important transport pathway of estrogens from agricultural land into the water environment is through surface runoff during storm events (Kjær et al. 2007; Jenkins et al. 2008; Dutta et al. 2010; Gall et al. 2011). Rainfall events of high intensities usually induce large estrogen mass loads into water (Kjær et al. 2007; Dutta et al. 2010; Gall et al. 2011).

Several studies have tried to quantify hormone loss in surface runoff during storm events. Gall et al. (2015) used an empirical model to estimate estrogen mass loads in surface runoff. Jones et al. (2014) used a similar empirical model to estimate the mass loads of the synthetic anabolic-androgenic steroid trenbolone, which is chemically similar to estrogen, in surface runoff. Lee et al. (2015) employed a Bayesian network model for estrogen transport. However, a modeling framework that quantifies the cause-and-response relationship and tracks the fate and transport of estrogens from agricultural land to receiving water is still incomplete due to three reasons: first, the impact of the interconversion of hormones during attenuation has not been investigated in studies on transport of estrogens; second, Gall’s and Jones’ studies did not concurrently investigate the effects of the surface runoff and the rainfall depth on the mass loads of steroids; and third, the wash-off model, a widely used model for transport of chemicals by surface runoff, has not been applied to estrogens yet.

The objective of this study was to quantify the pathway of estrogens from agricultural land to the receiving water following rainfall events. This study adopted a simple model, the wash-off model for the export of three prevalent manure-borne estrogens, estrone (E1), 17β-estradiol (E2β) and 17α-estradiol (E2α), from an agroecosystem. Data reported in the most recent literature were used to calibrate
the model. This study then compared the performance of the wash-off model to an empirical model which has been used for estrogen transport in previous studies.

METHODS

Development of models

The total mass of estrogen applied to the agricultural land can be estimated by multiplying the manure or biosolids application rate by the initial estrogen content in the manure or the biosolids. The initial estrogen content in fresh manure or biosolids is usually higher than that in stored manure or biosolids. The application rate of manure or biosolids can be determined based on nutrient requirements for the crops (Dutta et al. 2010). During the dry periods after land application, estrogens on agricultural land undergo an attenuation process that includes sorption to solids, biodegradation, photodegradation, and plant uptake (Das et al. 2004; Bradley et al. 2009; Caupos et al. 2011; Card et al. 2012). In addition, an interconversion exists among estrogens during the attenuation process and E1 is an intermediate of estrogen degradation (Goeppert et al. 2014). E1 works as the degradation intermediate of E2α and E2β, and these three compounds can convert to any of the others during attenuation (Mansell et al. 2011; Zheng et al. 2012). The complex attenuation and conversion process of E2α, E2β and E1 on land during dry weather can be described by the equations below (Zheng et al. 2012):

\[
\frac{dS_{E2\alpha}}{dt} = -k_{E2\alpha,E1}S_{E2\alpha} + k_{E1,E2\alpha}S_{E1}
\]

(1)

\[
\frac{dS_{E2\beta}}{dt} = -k_{E2\beta,E1}S_{E2\beta} + k_{E1,E2\beta}S_{E1}
\]

(2)

\[
\frac{dS_{E1}}{dt} = k_{E2\alpha,E1}S_{E2\alpha} + k_{E2\beta,E1}S_{E2\beta} - k_{E1,E2\alpha}S_{E1} - k_{E1,E2\beta}S_{E1}
\]

(3)

where, \(S_{E2\alpha}, S_{E2\beta}\), and \(S_{E1}\) are the total mass of E2α, E2β, and E1 applied to the agricultural land (μg), respectively; \(k_{E2\alpha,E1}\) is the transformation rate of E2α to E1 (day⁻¹); \(k_{E2\beta,E1}\) is the transformation rate of E2β to E1 (day⁻¹); \(k_{E1,E2\alpha}\) is the transformation rate of E1 to E2α (day⁻¹); \(k_{E1,E2\beta}\) is the transformation rate of E1 to E2β (day⁻¹), and \(t\) is time (day). The above equations can be solved using the Laplace transform and the solutions are attached in the Supporting Information (SI) (available with the online version of this paper) (Zheng et al. 2012).

Estrogens accumulated on land are transported to aquatic systems during rainfall events. Studies have proven that the estrogen mass transported by storm events is highly related to the rainfall amount (Yang et al. 2012; Jones et al. 2014). The Soil Conservation Service (SCS) rainfall-runoff model is widely used to estimate surface runoff during storm events (NRCS 2010):

\[
Q = \frac{(I - 0.2((2540/CN) - 25.4))^2}{I + 0.8((2540/CN) - 25.4)} \times A \times 10
\]

(4)

where, \(I\) is the measured rainfall intensity (cm/min); \(Q\) is the surface runoff (L/min); \(A\) is the land area of the agricultural land (m²); CN is the curve number, a parameter used in hydrology to predict direct runoff; and CN is a function of the soil type, hydrologic conditions, land use and the soil treatment.

The wash-off model, which has been widely used for transport of chemicals by surface runoff, is adopted to track the transport of estrogens following rainfall events (Shaw et al. 2009; Hossain et al. 2011):

\[
\frac{dS}{dQ} = -k_s S
\]

(5)

where, \(k_s\) is the wash-off coefficient (min L⁻¹).

Integrating Equation (5) yields:

\[
M = S[1 - \exp(-k_s \times Q)]
\]

(6)

where, \(M\) is the total mass of estrogens flushed from the land surface by surface runoff during storm events.

In addition to the wash-off model, an empirical model has been used to estimate the mass of hormones exported during rainfall events (Jones et al. 2014; Gall et al. 2015):

\[
M = c(SQ)^d
\]

(7)

where, \(c\) and \(d\) are dimensionless constants.

Model validation

Data

The data reported by Yang et al. (2012) were used to evaluate the performance of the wash-off and empirical models in this study. Yang et al. (2012) assessed the potential for
runoff of hormones and sterols, including androgens, estrogens, and progestogens from three adjacent agricultural test plots (Plots 1, 2 and 3). The area of each plot was 6 m² and the soil types of the study area were mainly classified as Vona loamy sand and Vona sandy loam. Yang's study modeled four identical precipitation events with an intensity of 65 mm and 1-hour duration 5 days before the biosolids application, as well as 1 day, 8 days and 35 days after the application. From each plot, the runoff rates and the hormone mass loads in surface water flow during artificial events on Day 1, Day 8 and Day 35 were measured and recorded. Even though these artificial precipitations were of the same intensity, the measured surface flow rate greatly varied due to the variation of antecedent moisture content (AMC). The variations of AMC on these three days were caused by the interference of the natural storm events and the effects of the previous artificial events. In this study, the mass loads of E1, E2β, and E2α in surface water flow reported on Days 1 and 8 were used to quantify key model parameters, and the mass loads of Day 35 were used to validate the models.

Derivation of model parameters

The transformation rates of estrogens were obtained from Zheng et al. (2013). The CN values were determined by fitting the SCS model to the measured flow rate curve. The measured and simulated flow rates using the SCS model are illustrated in Figure 1, and the derived CN values are summarized in Table S1 in SI (available online). Low r²-values for Day 1 indicate that the SCS model fails to catch the low flows and has a better performance for high flows. Besides, as shown in Figure 1, the measured flow rates on Day 8 from Plot 1 showed a sudden decrease after 25 minutes, and this observation cannot be explained by the SCS model. However, the SCS model overall effectively simulates the measured flow rate during the artificial rainfall events, with r²-values higher than 0.90 in most cases.

The calculated total masses of three estrogens on the agricultural land over time using Equations S4 to S10 in SI (available online), the solutions to Equations (1)–(3), are illustrated in Figure 2. The mass of E1 decreases after

![Figure 1](https://iwaponline.com/wst/article-pdf/77/10/2474/234909/wst077102474.pdf)

**Figure 1** | Simulated and measured surface runoff at three plots on Days 1, 8 and 35: the squares, circles, and triangles denote the measured surface runoff at Plot 1, Plot 2 and Plot 3, respectively; the short-dashed, dashed, and solid lines denote the surface runoff simulated using Equation (4) at Plot 1, Plot 2 and Plot 3, respectively. (Data from Yang et al. 2012.)

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![Figure 2](https://iwaponline.com/wst/article-pdf/77/10/2474/234909/wst077102474.pdf)

**Figure 2** | The calculated mass of estrogens at each plot after land application of biosolids using the model described by Equations S4 to S10 with interconversion of E1, E2α, and E2β.
the biosolids land application, while the masses of E2α and E2β increase as a result of the E1 transformation. Finally, equilibrium is reached among the three estrogens as they approach a steady state.

Model coefficients $k_r$, $c$, and $d$ were estimated by linear regression using the measured data. For the wash-off model, Equation (6) can be rewritten as follows:

$$\ln \left(1 - \frac{M}{S}\right) = -k_r Q$$ (8)

For the empirical model, Equation (7) can be rewritten as follows:

$$\ln(M) = d\ln(QS) + \ln(c)$$ (9)

A linear regression analysis was performed using the measured mass loads, measured surface runoff and the calculated mass storage on Days 1 and 8. The results and regression equations are summarized in Figure 3. Although the linear regression of the wash-off model has poor performance for E2α with a low $r^2$-value of 0.14, the linear regression shows good overall performance with $r^2$-values higher than 0.80 for E1 and E2β. The parameters derived and collected as described above are summarized in Table 1. Based on calculation results, $k_r$ values are constant for these three estrogens, varying from 0.00015 to 0.00021 min/cm, while the magnitudes of $c$ and $d$ values change drastically for these three estrogens.

### RESULTS AND DISCUSSION

The derived coefficients were applied to the wash-off and empirical models to estimate the mass loads of three estrogens from three plots on Day 35 to validate and evaluate the predicted performance of the two models. A comparison of the estimated and measured mass loads of E1, E2α, and E2β by the two models is summarized in Table 2. The empirical model shows higher $r^2$-values for E1 and E2β than the wash-off model, and the wash-off model shows a higher $r^2$-value for E2α than the empirical model. The $r^2$-values for E1 and E2β of both the models are higher than

| Table 1 | Parameters used for modeling |
|------------------|------------------|---|---|---|
| Parameter | Unit | Value | Source |
| $k_{E2\alpha,E1}$ | day$^{-1}$ | 0.076 | Zheng et al. (2012) |
| $k_{E2\beta,E1}$ | day$^{-1}$ | 0.22 | Zheng et al. (2012) |
| $k_{E1,E2\alpha}$ | day$^{-1}$ | 0.013 | Zheng et al. (2012) |
| $k_{E1,E2\beta}$ | day$^{-1}$ | 0.058 | Zheng et al. (2012) |
| $k_r,E1$ | min/L | 0.00015 | by model calibration |
| $k_r,E2\alpha$ | min/L | 0.00021 | by model calibration |
| $k_r,E2\beta$ | min/L | 0.00016 | by model calibration |
| $c_{E1}$ | – | $1.2 \times 10^{-8}$ | by model calibration |
| $c_{E2\alpha}$ | – | 0.0053 | by model calibration |
| $c_{E2\beta}$ | – | 0.00012 | by model calibration |
| $d_{E1}$ | – | 1.8 | by model calibration |
| $d_{E2\alpha}$ | – | 0.64 | by model calibration |
| $d_{E2\beta}$ | – | 1.0 | by model calibration |

![Figure 3](https://iwaponline.com/wst/article-pdf/77/10/2474/234909/wst077102474.pdf)
0.90, which indicates that both models are better at predicting the mass loads of E1 and E2β than E2α. The comparable $r^2$-values show that the empirical and wash-off models have similar abilities for estimating the mass loads for the three estrogens.

To evaluate the overall performance of the two models during the whole study period, the simulated mass loads and the measured values on Day 1, Day 8, and Day 35 are illustrated in Figure 4. Simulated results of both models match the measured values during rainfall events. On Days 1 and 35 with low flows, the difference between the simulated results of the two models is not significant. Conversely, the difference between the simulation results of the two models is larger on Day 8 with high flows, especially for E1 and E2α. The comparison of the two models is illustrated in Figure 5. In general, a greater overlap between the fitted line and the 45° line indicates a better performance. All of the fitted lines for the wash-off model for all three estrogens are closer to the 45° line than those of the empirical model. Thus, for this specific case, the wash-off model shows a better performance in predicting the mass loads of E1, E2α, and E2β than the empirical model.

A statistical analysis was conducted to evaluate the performance of the empirical model and the wash-off model on the transport of estrogens during rainfall events. The numerical difference between the modeled and measured estrogen mass loads was calculated first, then the difference between these two models was analyzed. $P$-values for the difference between the simulated and the

<table>
<thead>
<tr>
<th>Table 2</th>
<th>The coefficient of determination ($r^2$) for the measured and estimated mass load of three estrogens by two models from three plots on Day 35</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Empirical model and observed data</td>
</tr>
<tr>
<td>E1</td>
<td>0.95</td>
</tr>
<tr>
<td>E2β</td>
<td>0.94</td>
</tr>
<tr>
<td>E2α</td>
<td>0.64</td>
</tr>
</tbody>
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Figure 4 | Simulated and measured mass loads of estrogens during rainfall events from three plots: the squares, circles, and triangles denote the measured mass loads on Days 1, 8 and 35, respectively; the solid and dashed lines denote the mass loads simulated by the empirical and wash-off model, respectively. (Data from Yang et al. 2012.)
measured masses are summarized in the first two columns in Table 3. The empirical model has the highest P-value for E2β and the lowest P-value for E2α. The wash-off model has the highest P-value for E1 and the lowest P-value for E2α. The P-values for the difference between the simulation results of these two models are summarized in the third column in Table 3. As shown in Table 3, the P-value is low for E2β and E2α, indicating that there is a large statistical difference in the performance between the two models for E2β and E2α. Both the wash-off and empirical models had large variations from the true values, resulting in large differences between these two models. The numerical accuracy of these two models depends on the parameters used in this study. For example, the actual attenuation rate of estrogens varies with the environment, as it is affected by several factors, such as the temperature, estrogen concentrations and solar radiation (Bradley et al. 2009; Chowdhury et al. 2011). However, the attenuation rates of the three estrogens were assumed to be constant in this study. In addition, model coefficients are sensitive to the environment, such as soil properties, and the accuracy of the model coefficient estimation might be impaired by the sparse data used in this study. Furthermore, the actual interconversion of estrogens involves other estrogens rather than just the three investigated in this study, such as the conjugated estrogens, and thus might be more complicated than hypothesized in this study (Bai et al. 2015).

In general, both models do well in estimating the estrogen loads exported by surface runoff from agricultural land. Compared to the empirical model, the wash-off model performs better when applied to this specific case. Additionally, the wash-off model is more compatible with hydrological modeling software such as HSPF for large-scale application of estrogen modeling (Zhao & Lung 2017). In general, the performances of the wash-off and empirical models can be affected by several factors, such as the estrogen type, data quality, and surface flow rates. Thus, this comparison of results only applies to this specific study and a more general conclusion comparing these two models requires additional studies.
CONCLUSIONS

This study compared two simple models, the wash-off and empirical models, to investigate the transport of estrogens from agricultural land by surface runoff during rainfall events. The data reported by Yang et al. (2012) were used to evaluate the performance of the wash-off and empirical models. Study results prove that the wash-off model is suitable for modeling the transport of estrogens following rainfall events. While both models can closely simulate the mass loads of estrogens during rainfall events, the wash-off model is more powerful as it has the ability to simulate the mass of all three estrogens. Compared to the empirical model, the wash-off model is more compatible with hydrological modeling software such as HSPF for large-scale modeling. This study also indicates that the interconversion of estrogens affects the mass loads of each estrogen and thus must be considered. Due to the fact that the performances of the wash-off and empirical models are affected by factors such as the estrogen type, data quality, and surface flow rates, more studies are required to get a more general conclusion comparing these two models.

SUPPORTING INFORMATION

Some related formulas and tables are summarized in the Supporting Information, available with the online version of this paper.

REFERENCES


from manure-treated structured soils. *Environmental Science & Technology* 41 (11), 3911–3917.

First received 16 August 2017; accepted in revised form 20 April 2018. Available online 2 May 2018.